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## **Nanocatalysis: Academic discipline and industrial realities**

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**Abstract:** Nanotechnology plays a central role in both academic research and industrial applications. Nanoenabled products are not only found in consumer markets, but also importantly in business to business markets (B2B). One of the oldest application areas of nanotechnology is nanocatalysis—an excellent example for such a B2B market. Several existing reviews illustrate the scientific developments in the field of nanocatalysis. The goal of the present review is to provide an up-to-date picture of academic research and to extend this picture by an industrial and economic perspective. We therefore conducted an extensive search on several scientific databases and we further analyzed more than 1,500 nanocatalysis-related patents and numerous market studies. We found that scientists today are able to prepare nanocatalysts with superior characteristics regarding activity, selectivity, durability, and recoverability, which will contribute to solve current environmental, social, and industrial problems. In industry, the potential of nanocatalysis is recognized, clearly reflected by the increasing number of nanocatalysis-related patents and products on the market. The current nanocatalysis research in academic and industrial laboratories will therefore enable a wealth of future applications in the industry.

DOI: <https://doi.org/10.1155/2014/324089>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-106225>

Journal Article

Published Version

Originally published at:

Olveira, Sandro; Forster, Simon P; Seeger, Stefan (2014). Nanocatalysis: Academic discipline and industrial realities. *Journal of Nanotechnology*, 2014:324089.

DOI: <https://doi.org/10.1155/2014/324089>

## Review Article

# Nanocatalysis: Academic Discipline and Industrial Realities

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Received 24 July 2013; Revised 30 October 2013; Accepted 18 December 2013; Published 17 February 2014

Academic Editor: Carlos R. Cabrera

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Nanotechnology plays a central role in both academic research and industrial applications. Nanoenabled products are not only found in consumer markets, but also importantly in business to business markets (B2B). One of the oldest application areas of nanotechnology is nanocatalysis—an excellent example for such a B2B market. Several existing reviews illustrate the scientific developments in the field of nanocatalysis. The goal of the present review is to provide an up-to-date picture of academic research and to extend this picture by an industrial and economic perspective. We therefore conducted an extensive search on several scientific databases and we further analyzed more than 1,500 nanocatalysis-related patents and numerous market studies. We found that scientists today are able to prepare nanocatalysts with superior characteristics regarding activity, selectivity, durability, and recoverability, which will contribute to solve current environmental, social, and industrial problems. In industry, the potential of nanocatalysis is recognized, clearly reflected by the increasing number of nanocatalysis-related patents and products on the market. The current nanocatalysis research in academic and industrial laboratories will therefore enable a wealth of future applications in the industry.

## 1. Introduction

Nanoscience is considered as one of the key technology areas of the 21st century. An indicator for the tremendous research interest in this field is the annual number of publications on nanotechnology, which increased steadily since two decades (an illustration is provided in Figure 1). Due to the unique properties of nanoengineered materials, they are seen by many authors as having a huge potential in various application areas, for example, for intelligent food packaging and pathogen detection [1, 2], for targeted drug delivery and blood purification [3, 4], for the production of antibacterial and superhydrophobic textiles [5, 6], and for self-cleaning and light-transmission regulating windows [7, 8]. However, regarding consumer markets, the number of nanoenabled products is not yet as considerable as might be inferred from the large amount of publications in the field [9]. This inference might, however, not be applicable to the business to business (B2B) market for nanotechnology.

One of the oldest and most important application areas of nanotechnology is catalysis [15, 16], which is, too, an excellent example for such a B2B market for nanotechnology.

A difficulty in the analysis of B2B markets is that their characteristics are not as obvious to the nonprofessional observer as peculiarities of consumer markets [17].

The goal of the present paper, therefore, is to provide insight into the field of nanocatalysis. In contrast to existing reviews that focus mainly on scientific publications in this area [15, 18–23], the present paper features additionally an economic and industrial perspective. In the beginning of this review, we provide an overview of the science base of nanocatalysis. Firstly, the background of catalysis in general and its importance to green chemistry are outlined, followed by the most important principles guiding catalyst performance. In the next chapter, the synthesis of nanocatalysts is described, thereby discussing the differences between the two traditional approaches of homogeneous and heterogeneous catalysis leading to the novel fields of nanoparticle catalysts and porous nanocatalysts, respectively. In the second part of this review, we analyzed the current technological situation, by referring to the intellectual property situation, and we further illustrate the growth of the market for nanocatalysis.

To provide an up-to-date picture of academic research in the field, we conducted an extensive search on several public

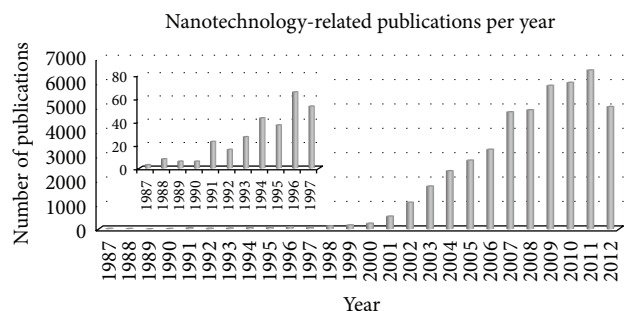


FIGURE 1: Development of the number of publications per year in the field of nanotechnology since 1987 (based on a research on Thomson Reuters' Web of Knowledge database; <http://www.webofknowledge.com/> last visited 16.01.2013 the value for 2012 is likely to increase as not all 2012 papers are already published online).

and restricted access online databases focusing on recent publications on nanocatalysts. To cover the industrial aspect of the present review, we evaluated more than 1,500 patents related to nanocatalysis from the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>). Further sources include company websites and market analyses. For the search, we used a working definition for nanocatalysis to differentiate it from conventional catalysis; that is, we considered catalytically active materials comprising either particles smaller than 100 nm in at least one dimension or porous compounds having pore diameters not bigger than 100 nm. Furthermore, at least one element of the catalytic process (e.g., activity, efficiency, or catalyst recovery) has to be improved due to the size effect compared to larger-scale catalysts to be included in our sample.

## 2. Perspectives of Nanocatalysts

**2.1. Catalysis: Background.** The field of nanocatalysis is not as new as could be expected from the current nanohype [24]. Actually, its concept is known since the 1950s when the term nanotechnology was not even known [19, 25, 26]. Nanocatalysis combines the advantageous characteristics of both homogenous and heterogeneous catalyses, while reducing their respective drawbacks [21]. In homogeneous catalysis, the starting materials and the catalytic substance are brought together in the same phase, which ensures high catalytic activity and selectivity [27]. The former can be expressed with the turn over frequency (TOF), defined as the number of substrate molecules that are catalytically converted into product during a certain time period. The latter is indicated by the yield of the desired product [28]. However, the practical application of homogeneous catalysis is limited by the difficulties to separate the catalyst from the product after completion of the reaction [29]. In heterogeneous catalysis, the starting materials and the catalytic substance reside in different phases [30], thereby alleviating the separation of products and catalyst. A main drawback of traditional heterogeneous catalyst systems compared to their homogeneous counterparts is the reduced surface area that is accessible to reactant

molecules, thereby limiting their catalytic activities [31] and leading to an unnecessarily high consumption of expensive catalyst materials [20, 31]. One possible way to solve this problem is to increase the surface to volume ratio (S/V) by decreasing the size of the catalytically active material [32, 33]. A high S/V can be achieved by synthesizing specifically engineered catalysts on the nanoscale, which is however not sufficient to comply to our above working definition for nanocatalysts.

Nanosized materials show additional unique properties compared to the macroscale [34]. A prominent example is the unexpected catalytic activity of gold nanoparticles, which is not found with bulk gold [35–38].

Nanocatalysis, finally, combines the positive aspects of the two conventional catalytic methods described above. The key targets that are pursued with nanocatalysis are close to 100% selective reactions, extremely high activity, and excellent yield—all traditionally related to homogeneous catalysis—as well as enhanced products separation and catalyst recovery—typically associated with heterogeneous catalysts [17, 20, 21]. Some authors consider nanocatalysis as “semiheterogeneous” [39] or “soluble heterogeneous” [40] catalysis. In contrast to them, we want to define nanocatalysis as a distinct category, because it closes the gap between hetero- and homogeneous catalysis [19, 21, 22], while concomitantly requiring totally new synthetic approaches [30] and displaying unique characteristics [41].

As nanocatalysts are further expected to contribute to lower process energy consumption, longer lifetime of the catalyst systems and enhanced possibilities to isolate and reuse the active nanomaterials, they are prominent examples to illustrate the efforts towards “green chemistry” for which catalysis is regarded as one key element [19, 42].

**2.2. Nanocatalysis in Green Chemistry.** Green chemistry is generally accepted as “the design, development, and implementation of chemical processes and products to reduce or eliminate substances hazardous to human health and the environment” [43]. The idea of performing this kind of chemistry is gaining prominence amongst the players in the chemical industry, as today's major challenges are to achieve sustainable production processes, having lower energy consumption and less environmental impact. Additionally, greener production processes might also prove to be economically beneficial for the companies [11]. For instance, the price of platinum increased significantly since the year 2000, as illustrated in Figure 2, and therefore the recovery and reuse of such expensive precious metal catalysts are advisable [22].

The potential of this revolutionary philosophy is illustrated by several examples of commercialized green chemistry processes [44]. However, the total impact of this new way of doing chemistry is still slight compared to the conventional industrial processes [45]. The reason for that is that companies maximize profitability within the current policy limits, while keeping an eye on social acceptance. As established processes are often good enough to comply with the regulations, greener processes—although less

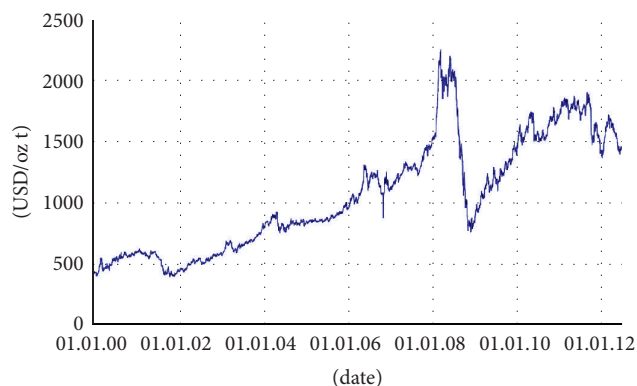


FIGURE 2: Development of the price of platinum (USD/oz t) in the past 12 years [10] (used with permission from <http://www.finanzen.net/>).

polluting—might not be considered for implementation: “new green chemistry processes will be introduced only if they can provide a payback quickly enough to be attractive to managers and investors” [11]. Thereby it should be noted that green chemistry is not merely targeted to lower energy consumption [11], but rather includes broad concepts regarding for example, waste minimization, usage of nontoxic reagents and other recommendations summarized by Anastas’ and Warner’s 12 principles of green chemistry [43]. As these 12 principles fall short of considering broader environmental impacts, arising from the entire life cycle of a product or process [46]; additionally 12 principles of green engineering were proposed [12]. We analyzed these 24 guidelines of green chemistry and engineering with regard to nanocatalysis. The results show that some nanocatalysts could potentially make an important contribution to the implementation of 13 out of these 24 principles. These relations are visualized in Figure 3 and will be discussed briefly in the following section, referencing patents and examples from the scientific literature.

- (i) Increased selectivities achieved by nanocatalysts compared to conventional reactions [47], like in the nanocatalytic hydrogenation of cyclohexanone [48] or in reforming processes [49], help to accomplish the first principle of green chemistry (corresponding to the second principle of green engineering): “It is better to prevent waste than to treat or clean up waste after it is formed.”
- (ii) Using nanocatalytic processes, which replace organic solvents by water [50, 51], is a formidable example for the third principle of green chemistry: “Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.”
- (iii) The fourth principle, “Chemical products should be designed to preserve efficacy of function while reducing toxicity,” should of course also be applied to the synthesis of nanocatalysts [52]. This is exemplified

by the synthesis of nontoxic ZnO nanoparticle catalysts [53] or by the stabilization of nanocatalysts by employing plant polyphenols [54].

- (iv) Nanocatalysts that render laborious separation steps unnecessary, such as magnetic nanoparticles [55, 56], illustrate one aspect of the fifth principle: “The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.” This elegant way of separation also fits the third principle of green engineering, which reads as follows: “Separation and purification operations should be designed to minimize energy consumption and materials use.”
- (v) For numerous chemical processes, harsh reaction conditions can be avoided by employing nanocatalysts, as, for example, in the hydrolysis of esters [57], as suggested by the sixth principle: “Synthetic methods should be conducted at ambient temperature and pressure.”
- (vi) Nanocatalysts have the potential to open direct reaction paths that were unachievable using traditional methods, such as in the direct synthesis of  $H_2O_2$  [58, 59], demonstrating the practicability of the eighth principle: “Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.”
- (vii) The ninth principle, “Catalytic reagents (as selective as possible) are superior to stoichiometric reagents,” is found, for example, in the advancement of the well-known Friedel-Crafts reaction by the introduction of a nanosized zeolite catalyst [60].
- (viii) With regard to the safety of chemical processes, mentioned in the last principle of green chemistry, “Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires,” nanocatalysts can make an important contribution, like in safer oxidation processes for organic molecules [61]. This example corresponds as well to the first principle of green engineering: “Designers need to strive to ensure that all material and energy inputs and outputs are as inherently nonhazardous as possible.”
- (ix) The fourth principle of green engineering is not equivalently represented in the 12 principles of green chemistry. It reads as follows: “Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.” A possible implementation of the suggestion is shown by an improved naphtha hydrogenation process that increases the octane number of products for a given catalyst loading [49].
- (x) The last of the 13 principles related to nanocatalysis is the eighth principle of green engineering: “Design for unnecessary capacity or capability (e.g., “one size

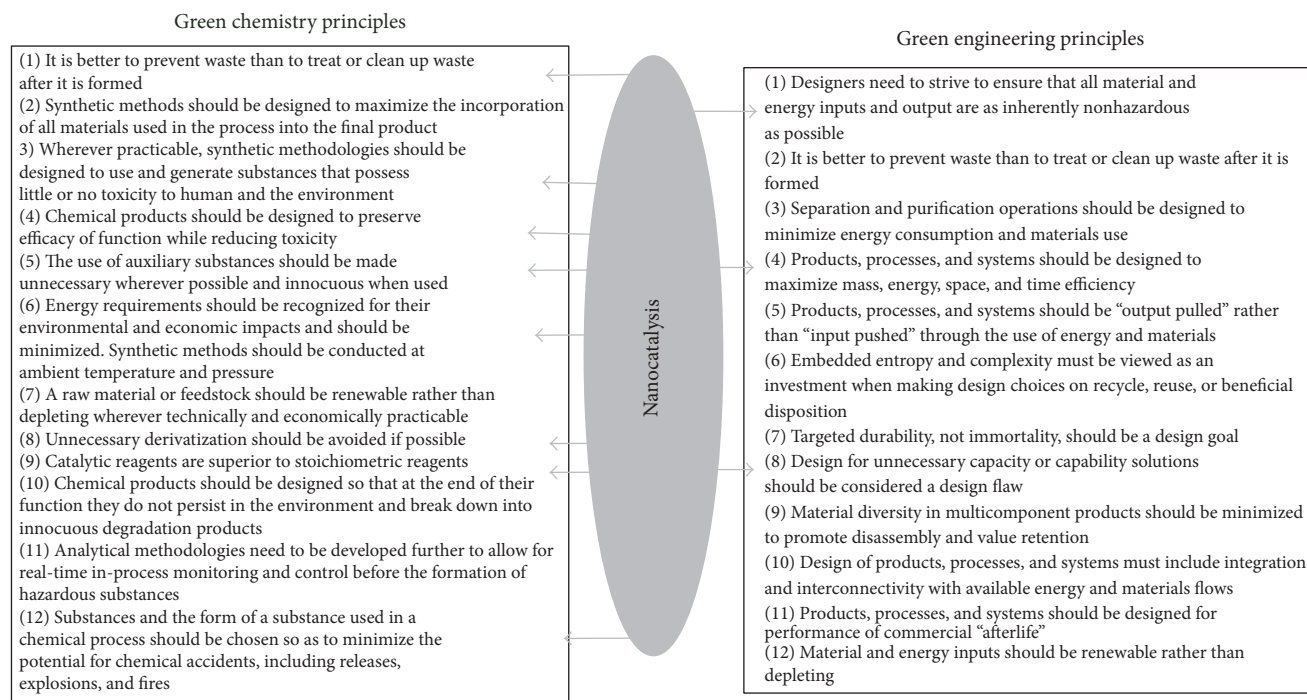


FIGURE 3: Potential contribution of nanocatalysis to green chemistry [11] and engineering [12].

fits all") solutions should be considered a design flaw." In this direction, carbon nanotubes are recognized to be a valuable catalyst support, which can be functionalized according to the desired catalytic activity [62–64].

The use of nanocatalysts to render chemistry greener as described in the examples above is important. However, we want to emphasize that not only the synthesis process for the products is relevant for green chemistry, but especially also the recovery and reusability of the nanocatalysts [20, 65]. Besides the mentioned magnetic nanocatalysts, nanoparticles in ionic liquids represent a further promising approach to solve the problem of catalyst separation [66]. One advantage of such systems is the facile recycling and high reusability without any drop in activity [67]. A further green aspect of ionic liquid/nanoparticle approaches compared to reactions in organic solvents is the low vapor pressure and the low miscibility with organic solutes, enabling easy isolation of volatile compounds [68–70]. Biphasic fluororous media represent a further promising technique for green catalysis [71].

### 3. Catalyst Performance

**3.1. Performance Dimensions.** An optimal nanocatalyst is expected to show superior performance in the following four dimensions: (a) selectivity, (b) activity, (c) durability, and (d) recoverability.

- (a) A selective catalyst produces ideally 100% of the desired product, even if competing reaction pathways would lead to thermodynamically more stable molecules. Like this, a tedious separation step can

be eliminated and the raw material is converted more efficiently to the product without generating unnecessary waste that has to be disposed of. From an economical point of view, the process costs can potentially be reduced.

- (b) Activity expresses how many molecules of raw material are converted to product molecules by the catalyst per unit of time. As mentioned previously, the so-called turnover frequency (TOF) is used as a measure for the activity. Conventional homogeneous catalysts display desirably high TOF in the range of  $0.3 \text{ s}^{-1}$  or higher, whereas heterogeneous catalysts are in the range of  $0.03 \text{ s}^{-1}$  or even lower [72]. Nanocatalytic systems are targeted to reach high TOF values as known from their analogous homogeneous systems. Considering industrial applications, high activities are favorable, as a higher output per time can be achieved leading to higher plant capacity utilizations.
- (c) The lifetime of a catalyst—its durability—is measured by the total number of catalytic cycles it can undergo until it needs to be replaced. A common value used in this context is the turnover number (TON), which denotes the total amount of product (in moles) that can be formed by a given amount (in moles) of catalyst [73]. Therefore, a highly durable catalyst enables the economic production of a larger quantity of the desired compound, before the process has to be interrupted for the replacement of the catalyst.
- (d) The major hindrance to the commercial application of a lot of promising homogeneous catalytic systems, successfully tested in the lab, is the recoverability of



the catalytically active substance. Therefore, an optimal nanocatalyst features an intrinsic system facilitating its separation from the reaction mixture and its reuse after termination of the reaction. The economic advantages are a reduction in needed amounts of expensive catalytic materials and an improvement in product quality, especially with regard to stringent regulations, for example, in the pharmaceutical sector.

**3.2. Influencing Factors.** The four dimensions mentioned above are strongly influenced by three factors, catalyst size, shape, and surface composition, which all have to be regarded when designing such an optimal catalyst [25, 47, 74–76]. An obvious consequence of reducing the size of catalysts to the nanoscale is that the relation of surface atoms to bulk atoms increases. Like this, more catalytically active sites are accessible for substrate molecules, which can lead to an increase in TOF [19, 20]. Further, the surface atoms can be classified into two broad categories—the face atoms typically having a high coordination number as opposed to the edges and corner atoms typically exhibiting lower coordination numbers [77]. The relation of catalytic activity and nanoparticle size is influenced markedly by the proportion of these different surface atoms [77]. As mentioned earlier in this review, size reductions of materials do not merely lead to an increase in S/V but evoke novel properties differing from their macroscopic counterparts. A well-known example for this size effect is gold that becomes catalytically active in the nanoscale [78]. Importantly, however, it should be noted that decreasing size does not always lead to improved characteristics, as, for example, the proportion of edge and corner atoms increases as the nanoparticles shrink [77]. For instance, in the direct synthesis of hydrogen peroxide decreasing the size of the catalyst nanoparticles from 4 to 2 nm dramatically changes the product selectivity from  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$  [26]. Another example, showing the size dependent selectivity is reported by Hayashi et al., who tested the catalytic activity of gold nanoparticles in the reaction of propylene with  $\text{O}_2$  and  $\text{H}_2$  [79]: if the particle size is smaller than 2 nm, propane is formed instead of propylene oxide.

Considering the second factor, catalyst shape, Narayanan and El-Sayed showed that the distribution of the surface atoms in platinum nanoparticles strongly impacts the activity of the nanocatalyst system [80]. For their study, they compared the ability of tetrahedral, cubic, and “near spherical” particles to catalyze the reaction of hexacyanoferrate (III) and thiosulfate ions and found that the catalytic activity correlates with the amount of atoms at corners and edges. Therefore, although having the same size, tetrahedral particles—featuring a larger amount of edges and corners—are considerably more active than spherical ones.

Besides activity, selectivity can also be tuned by changing the shape of the nanocatalyst as demonstrated, for example, by Lee et al. [81]. The result of their investigation is that Pt nanoparticles with (111) faces favor the formation of cis-over trans-2-butene in their isomerization reaction, although the trans isomer is more stable thermodynamically. This

surprising change in reaction selectivity for same-sized Pt nanoparticles is only affected by the structure of the surfaces, which result from the modification of the respective particle shape.

Thus, as can be seen from the above examples, the selectivity exhibited by an optimal nanocatalyst depends on the catalyst size on the one hand and on catalyst shape on the other hand. Both effects are obviously interdependent, as was discussed, for example, for the selective furan hydrogenation [47]. However, it is important to note that the size and shape of metal nanocatalysts may change during a reaction, which influences the active sites [77].

Like size and shape, surface composition of the catalyst as the third factor also influences its activity and selectivity. Pool, for example, showed that the catalytic activity of  $\text{Co}_{13}$  toward hydrogen completely disappears when a vanadium atom replaces one of the Co atoms in the composition [82]. Furthermore, by coadsorbing molecules, such as electron donors or acceptors, to the surface of the catalyst, the activation energies of the different potential reaction pathways and therefore the respective selectivities can be influenced as the stabilities of the reaction intermediates are affected [47]. In addition to that, surface composition is an important contributor to nanocatalyst durability and recoverability. As nanoparticle catalysts have a high tendency to agglomerate, posing problems to durable catalytic activity, it is important to stabilize the catalytic system [83]. One possibility to enhance durability is the functionalization of the surface with capping agents, for example, polymers or surfactants [22]. By introducing further substituents to the surface, it is also possible to facilitate the recovery of the catalysts from the reaction medium after termination of the synthesis. A prominent example is the use of magnetic catalyst components, which allow the flawless separation of the catalyst from the medium with the aid of a magnetic field. Several procedures are described in the literature, for example, for hydrogen generation [84] or for the aqueous homocoupling of arylboronic acids [85], and some catalysts are even commercially available [17]. Another elegant way of recovering the catalyst from the reaction mixture is to render its surface pH sensitive. By adjusting the pH, the catalyst can be precipitated [65].

## 4. Synthesis of Nanocatalysts

**4.1. Progress in Preparation of Nanocatalysts.** In the past, particularly the characteristics activity and selectivity of the catalysts were optimized by a simple trial and error approach [26] without a clear understanding of the underlying influencing factors. The traditional synthesis methods did not allow for a precise control of nanocatalyst size and shape [86] and therefore “[t]he field of catalysis science is often criticized as being ad hoc and empirical” [25]. Today, activity, selectivity, durability, and recoverability can be influenced owing to the advances in nanoscience [16, 17, 87]. The size, shape, and surface compositions of nanocatalysts are designed and synthesized in a more precise way by adjusting the reaction conditions, such as reaction time, temperature and reactant concentrations [88, 89].

In general, nanocatalysts can be synthesized by either a top-down or bottom-up approach [20, 90]. As the name implies, the idea behind the top-down approach is to break bulk material down mechanically [91, 92], thermally [93], or chemically [94], into smaller and smaller particles. The top-down approach is criticized because of its inability to yield particles with uniform characteristics [95]. However, there are already improved procedures to control the size and surface composition more precisely [94]. The bottom-up approach involves the formation of nanocatalysts by reaction or agglomeration of suitable starting molecules with or without structure-directing agents [76]. This principle is used more commonly than the former approach [20], although it is rather disadvantageous both from an economical and environmental points of view, due to harsh reaction conditions employed and the use of expensive precursors and structure-directing agents [45, 96]. Nevertheless, it allows the synthesis of well-defined catalysts on the nanoscale, in regard to size, shape and surface composition [34, 97].

In the following part, we discriminate between nanoparticle catalysts and porous nanocatalysts, like other authors [17, 98], and discuss their respective production methods in more detail.

**4.2. Synthesis of Nanoparticle Catalysts.** Already in the 1850s, Faraday produced metal nanoparticles by the chemical reduction of the respective metal salts, which is still a common way in nanoparticle synthesis [99]. Later, in the 1920s metal nanoparticles were introduced to catalyze chemical reactions [100]. In a desire to reduce costs of large-scale catalytic systems, for example, in the refinery industry, researchers in the 1950s began to produce smaller catalytic particles in order to profit from the resulting advantageous characteristics described above [26]. Thereby, the size was lowered from 100 nm in the beginning to less than 1 nm today [101]. Both, top-down and bottom-up approaches are conceivable for the synthesis of nanoparticle catalysts. Numerous methods were developed, including rather conventional techniques like mechanical grinding or chemical breakdown of bulk material or electrochemical or solvothermal processing of precursor solutions [102, 103]. Further selected examples and innovative alternatives, such as microwave irradiation processing, resulting in catalysts of more precisely defined size and shape are listed in Table 1 [86, 104–106].

The two major problems in the synthesis and application of nanoparticle catalysts are their tendency to agglomerate associated with deterioration in their unique characteristics and the difficulties encountered in the catalyst recovery from the reaction mixture [20, 22, 107]. To overcome the aggregation problem, the nanoparticle catalysts can be deposited on different kinds of supports, such as carbon, graphite, and hydrogels [84, 86]. Li et al. used carbon nanotubes to support palladium nanoparticles in the catalytic reduction of 4-nitrophenol [62]. Alternatively, support-free nanocatalysts can be stabilized by using one of the three following methods, generally referred to as electrostatic, steric, and electrosteric stabilization [20]. Electrostatic stabilization is achieved by creating an electrical double layer around the

TABLE 1: Overview of top-down and bottom-up approaches used for the synthesis of nanoparticles (based on [26, 86, 99, 102–106]).

Top-down technologies	Bottom-up technologies
	(i) Sol-gel
	(ii) Chemical reduction of salts
(i) Mechanical grinding	(iii) Electrochemistry
(ii) Metal vapor	(iv) Solvothermal processing
(iii) Thermal breakdown	(v) Template-directed
(iv) Chemical breakdown	(vi) Precipitation
(v) Spontaneous chemisorption	(vii) Microemulsion
	(viii) Microwave irradiation
	(ix) Sonochemistry

nanoparticle catalyst with salts dissolved in the reaction mixture or by ionic liquids [107]. These double layers hinder the particles of coming too close to each other and therefore prevent aggregation. For instance, rhodium nanoparticles used in the catalytic hydrogenation of functionalized aromatic compounds were stabilized by ionic liquids [108]. Such a protective layer can also be formed by adsorbing macromolecules or other ligands, such as phosphines or thiols, to the particle surface, leading to steric repulsion. Léger et al., for example, stabilized rhodium nanoparticles with various bipyridine ligands, for their use as hydrogenation catalysts for arenes [109]. The third method, electrosteric stabilization, results from combining the effects of the two previous ones. Thereby, the surfaces are covered with surfactants containing polar head groups (for the electric double layer) and lipophilic side chains (for the steric repulsion) [107, 110] or polyoxoanions. Mévellec et al., for example, stabilized an iridium(0) nanocatalyst for the hydrogenation of arenes in a biphasic medium by using N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl)ammonium chloride salt as surfactant [111]. Hornstein and Finke, on the other hand, prepared a tetrabutylammonium- and polyoxoanion ( $P_2W_{15}Nb_3O_{62}^{9-}$ )-stabilized Ir(0) nanocatalyst [112]. Despite all the advantages of the above described stabilization methods, it has to be borne in mind that stability and activity of the catalytic nanoparticle are reciprocally related; that is, a nanoparticle withstanding even the harshest conditions is likely to be catalytically inactive [72, 113]. Within this trade-off it is nevertheless possible to obtain a stable and active nanocatalyst, by choosing stabilizers that are weakly bound to the active site but still offer good protection, for example, by electrosteric repulsion [72]. Yan et al. prove that a suitable stabilizer can optimize catalyst stability, while retaining high activity [110].

As mentioned above, beside nanoparticle aggregation the second challenge in the successful application of nanocatalyst particles is their efficient recovery from the reaction mixture. The recovery of used catalysts would be beneficial in two respects. On the one hand, catalytic nanomaterials, precious metals in particular, are very expensive. On the other hand, unrecovered catalysts are a major source of unwanted impurities, for example, in pharmaceutical products. The efficient separation of the catalyst from the reaction mixture could help to meet legal standards regarding impurities more easily [114]. To solve the recovery problem, the use of a magnetic

support for the catalytically active nanoparticles was proven to be effective [115–117]. Schätz et al., for example, synthesized a novel magnetic hybrid material as support for a palladium catalyst that can be easily recovered after use [118].

**4.3. Synthesis of Porous Nanocatalysts.** After discussing the synthesis, applications, and problems of nanoparticle catalysts, we will focus on the second major category of nanocatalysts: the porous nanocatalysts. These crystalline catalysts are characterized by clearly defined and regularly structured pores and channels on the nanoscale, wherein the catalytic processes take place [76, 119]. The confinement of the available space is beneficial in two respects: on the one hand, molecules that are too large are excluded from participating in the reaction and on the other hand, the regio- and stereoselectivity of the reaction process can be influenced by the pore structure. For this class of catalytic systems the term “nanoreactors” was introduced [31, 120]. The most prominent representatives of this class are zeolitic frameworks, which are widely used in industrial catalysis [121]. While several different zeolites are naturally occurring, only the design and directed synthesis of artificial zeolitic frameworks, which was initiated in 1956 at Union Carbide by Reed and Breck with the production of zeolite A, paved the way for their widespread application in industry [122, 123]. This breakthrough was possible by the first preparation of a synthetic zeolite by Barrer in the late 1940s [124, 125]. Due to the rapid development of this field, more than 200 naturally occurring as well as synthetic zeolites are known today [126], but only the synthetic ones are of major industrial significance [127]. Important structural elements of zeolites are  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons [128], which can be linked to form secondary building units. Some zeolites consist of polyhedra made up by these secondary building units [127]. The basic approaches to prepare zeolites, already introduced by Barrer, are known as the hydrothermal synthetic techniques [129]. They commonly involve reaction of precursors, consisting of silica and optional alumina sources, in a basic or acidic aqueous environment. The following crystallization and product recovery steps complete the synthetic process. The entire procedure is performed in a closed system above 300 K and 1 bar. Reactions performed in the temperature range from 370 K to 510 K are classified as subcritical. Accordingly, reactions in the range from 510 K to over 1200 K with pressures up to 3000 bar are termed supercritical syntheses. Further preparation methods were developed based on the hydrothermal synthesis technique, such as solvothermal, ionothermal, microwave-assisted hydrothermal, microemulsion-based hydrothermal, and combinatorial synthetic routes [129].

Two problems exist in the synthesis and application of porous nanocatalysts in general and zeolites in particular. Firstly, to show catalytic activity, the inner surfaces of the porous catalysts often need to be functionalized, as, for example, silicates per se are normally unreactive [119, 130]. A widely applied method to render zeolitic frameworks catalytically active is to impregnate their interior surfaces with catalyst precursor solutions [30]. Johnson et al., for instance tied a chiral molecule to the inner walls of MCM-41

mesoporous silica to catalyze allylic amination of cinnamyl acetate [131], and Liu et al. used mesoporous SBA-15 as a support for vanadium oxide for the selective catalytic oxidative dehydrogenation of propane [132].

Secondly, diffusion of substrate molecules into the frameworks is often limited, especially when the dimensions of the pores and molecules are similar, so that not all active sites are used for catalysis [16]. In the last twenty years, zeolite researchers focused on the synthesis of ultra large-pore structures, which presents a possible solution to the problem of diffusion [76, 133]. More precisely, microporous active sites within the zeolites are interconnected by larger mesoporous frameworks. These comparably large pores allow substrates and products to diffuse in and out of the zeolite more freely [16]. Several examples for functionalizations of the inner walls of mesoporous zeolite are reported in the literature. Yang et al. anchored palladium complexes to mesoporous MCM-41 via dicyano-linkers as a new kind of catalyst for the Heck reaction [134]. Tsai et al. also report a novel moiety able to catalyze the Heck reaction. In their approach, they tied a palladium bipyridyl complex to the inside of MCM-41 channels [135]. Both catalysts show high stabilities having turnover numbers up to  $10^6$ .

**4.4. Future Applications of Nanocatalysts.** After presenting the synthesis and applications of both nanoparticles and nanoporous materials as catalysts, we will now provide selected examples for several different future applications of nanocatalysts. Like this we show broad range of potential uses of such catalysts. Several of them combine the advantages of particulate and porous nanocatalysts, while concomitantly reducing some of their drawbacks.

Pan et al. used the inner walls of carbon nanotubes as support for rhodium particles, which are catalytically active in the production of ethanol from CO and  $\text{H}_2$ . They found that the overall ethanol formation rate inside the carbon nanotubes is an order of magnitude higher compared to the analogous reaction on the outer wall of the tubes [136]. In another example, single-step hydrogenations of, for example, benzene to cyclohexene or cyclohexane can be catalyzed by bimetallic nanoparticles anchored within mesoporous silica exhibiting high performance [137]. These examples nicely show that the already superior activity of nanoparticle catalysts can even be multiplied when linking them to the advantageous characteristics of porous nanomaterials.

Further promising approaches, which gained some prominence in recent research, are core-shell nanocatalysts, also showing high performance. Wu et al., for example, confined gold nanocatalysts to hollow nanoscale silica shells for the reduction of 4-nitrophenol with high catalytic activity. A special property of this catalytic system is its resistance towards inactivation caused by strongly adsorbing molecules [138]. Joo et al. prepared a core-shell nanocatalyst consisting of a platinum core and a mesoporous silica shell particularly suitable for high temperature reactions. The shell offers direct access for the substrates to the catalytically active core but nevertheless protects the core up to 1000 K occurring, for example, in CO oxidation reactions [139].



Furthermore, several authors proposed magnetic core-shell nanosystems with regard to the recovery of the catalytically active moieties [140–144]. Mi et al. designed such a catalytic system with an iron oxide core and a shell consisting of magnesium, aluminum, and gold compounds for the oxidation of 1-phenylethanol [140]. It is also conceivable to use a component in a core-shell system that combines both catalytic activity and magnetic recoverability, as demonstrated by Park et al. They synthesized a nanoreactor, built from a Ni core protected from sintering at high temperatures by a SiO<sub>2</sub> shell, for the steam reforming of methane [143]. In all cited examples the core-shell catalysts can be flawlessly and effectively recovered from the reaction mixture by application of an external magnetic field.

It is obvious that all the nanocatalyst technologies presented above have the potential to play a crucial role in various application fields, such as in the synthesis of widely used organic compounds, in the “H<sub>2</sub> economy,” in oil refining, in pollution control and in biological nanosensor applications [18, 19, 22, 25, 26, 31, 34, 45, 84, 138, 145–150]. In the following part, we will present selected interesting examples that point into these directions.

Tedsree et al. discuss the unconventional idea of small, portable fuel cells based on hydrogen generation from formic acid catalyzed by gold-palladium core-shell structures [149]. In the same area, Wang et al. envisioned the use of nanocatalysts for biofuel cells powered by glucose [147]. Biological applications of nanocatalysts can also be extended to the broad field of bionanosensors, for example, for diagnostic or therapeutic purposes [26, 138]. A totally new approach in the design and use of nanocatalysts is also related to biochemistry: some researchers chose a bionic strategy by taking enzymes as role models for the synthesis of nanocatalysts. One goal of these efforts is, for example, the enabling of catalytic reactions performed at room temperature [31].

A major challenge for the oil industry is the deteriorating quality of crude oil feedstock due to the increase in the percentage of long-chain hydrocarbons. Novel nanocatalysts able to cope with those heavy substrates are expected to solve this problem. Concomitantly, metal-free nanocatalysts are developed to counter the sharp rise in rare earth metal prices [146].

Despite these visions of a bright future for nanocatalysis, it has to be emphasized that the risks posed to both the environment and human health are still poorly understood based on the currently available data [151–155]. Especially for the consumer market there is a need to explore toxicity and long-term effects of nanomaterials more thoroughly as soon as possible, because more than 600 nanoproducts are already on the market [156, 157].

## 5. Industrial Interest in Nanocatalyst Applications

**5.1. Nanocatalysis: Intellectual Property Situation.** Still, after the presentation of the advances in nanocatalysis research, the question remains to what extent industrial companies are interested in nanocatalysts. In the following part, we want to shed some light on recent developments in the industry by

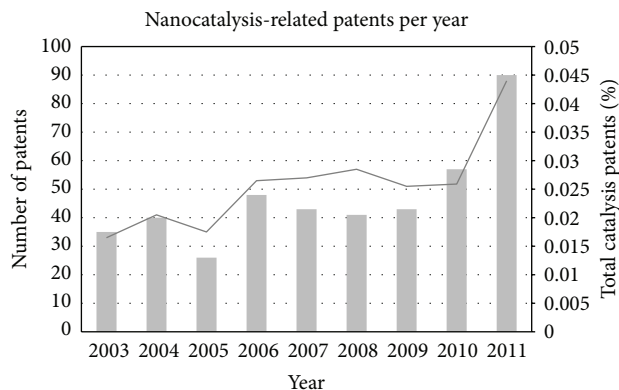


FIGURE 4: Development of number of patents granted in the field of nanocatalysis since 2003 (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

an extensive analysis of more than 1,500 nanocatalysis-related patents. These were retrieved by a search on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>). The keywords nano, catalyst, nanoparticle, nanocomposite, mesoporous, nanoscale, particle, nanocatalyst, nanocatalysis and catalytic material were used in various combinations for full-text searches and the truncated terms nano\$ and catal\$ for abstract searches (\$ indicates truncation for the search engine). 475 out of the more than 1,500 analyzed patents were found to comply with our working definition for nanocatalysts stated in the beginning of this paper (Table S1 Supplementary Material available online at <http://dx.doi.org/10.1155/2014/324089>). We decided to categorize these 475 patents according to the following categories: year of granting, application field, and assignee. The results of this search presented in the following show the general interest of industry in nanocatalysis but do not necessarily reflect the extent of application of such catalysts in industry.

The development of the number of nanocatalysis-related patents granted in a given year shows the same overall trend as the nanotechnology-related publications, which was demonstrated in the beginning of this paper: although the year-to-year comparison is subject to minor fluctuations, there is a noticeable increase in the total number of patents from 2003 to 2011 as illustrated in Figure 4. Additionally, the graph shows the development of the percentage of nanocatalysis-patents in relation to the total number of patents in the field of catalysis (these numbers were determined by an abstract search on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) with the keywords catalyst and catalysis).

A more detailed analysis of the patents allowed us to determine the following six major industrial application fields for nanocatalysts: combustion, fuel cell/electrochemistry, hydrocarbon processing/cracking, templating, various chemical processes, and the category not specified. We included patents related to the enhancement of combustion processes or for the treatment of combustion exhaust gases in the

combustion group. For instance, Headwaters patented organically complexed nanocatalyst compositions to be mixed with carbon-containing fuels reducing the amount of CO and hydrocarbons released by combustion [158]. To purify engine exhaust gases Toyota developed heat-resistant nanoporous catalysts comprising two or more kinds of first metal oxides [159]. The category fuel cell/electrochemistry includes patented innovations related to the improvement of electrochemical reactions as they are typically found in fuel cell applications. Samsung, for example, developed catalysts consisting of metal nanoparticles anchored to a carbon support to increase fuel efficiency and energy density of fuel cells [160].

All nanocatalysts designed for the use in hydrocarbon processing and crude oil cracking were summarized to a single group. Examples include a mesoporous structure incorporating catalytically active heteroatoms patented by Lummus Technology for the use in a variety of carbon feedstock upgrading reactions [161] or a mesoporous nanocatalyst invented by ExxonMobil for fluid catalytic cracking to reduce coke and light gas formation [162].

The fourth category, templating, contains patents related to the synthesis of nanostructures templated by nanocatalysts. A prominent application in this field is the production of carbon nanotubes as exemplified by Honda's patent revealing the application of supported metal nanoparticles to grow single-walled carbon nanotubes [163].

All patents with defined application fields not related to the four previous categories were appropriated to various chemical processes. Chiefly, the disclosed nanocatalysts are applied in organic chemical syntheses, such as in the preparations of olefins by employing nanoporous ceramic oxides catalysts [164] or in the catalytic alkylation of monocyclic aromatic compounds using mesoporous zeolites [165]. The last category, not specified, includes all patents that describe the synthesis of nanocatalysts, but without providing a specific application field. A patent granted to Nanostellar, for example, details the preparation of multicomponent catalysts with nanometer sized particles [166].

After categorizing all the 475 patents into the six categories listed above, it can be seen that hydrocarbon processing/cracking and various chemical processes each claim 23 percent of all patents analyzed in detail. The other four categories have an equal share of approximately 13 to 15 percent as illustrated in Figure 5.

It can be inferred from Figure 5 that chemical conversion reactions employing nanocatalysts, either for the processing of hydrocarbon feedstock or in synthesis of (organic) molecules, are a major interest in the industry. However, when the numbers of patents in each of the six application fields are plotted over time as in Figure 6, the buoyancy of the categories combustion, fuel cell/electrochemistry, and templating is discernible. The other three categories show either a lateral or downward movement.

To determine in which of the six application fields the individual assignees are most active, we plotted the number of patents in the six categories for each company in Figure 7. Thereby, only companies with five or more awarded patents

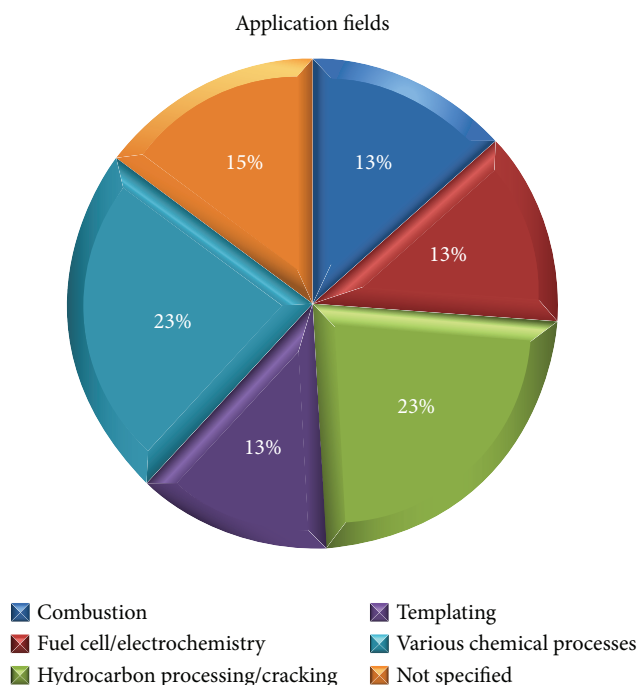


FIGURE 5: Application fields of patents related to nanocatalysis (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

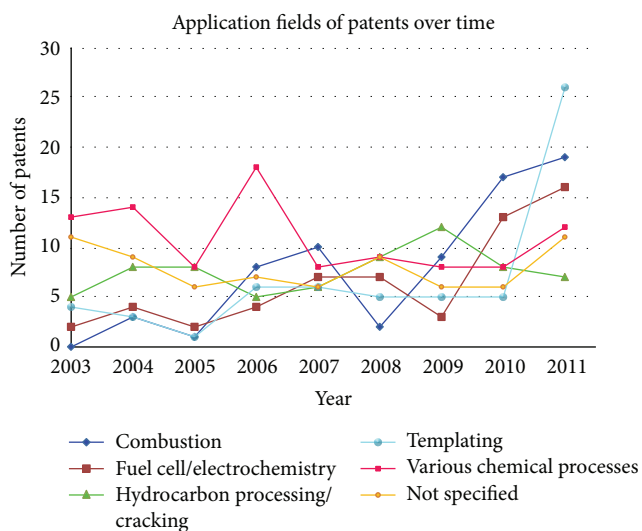


FIGURE 6: Development of application fields of patents related to nanocatalysis (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

were considered. The graph shows that the companies Exxon-Mobil, Philip Morris and Headwaters were granted the majority of all patents in our sample. It is obvious from Figure 7 that a lot of companies are clearly targeted toward one respective application field; for example, almost all catalysis-related patents owned by ExxonMobil, Lummus, ConocoPhillips,

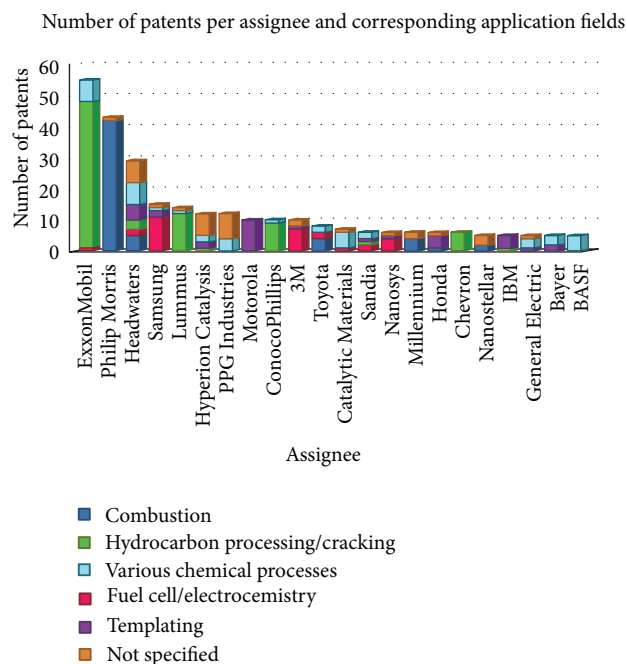


FIGURE 7: Major assignees of patents related to nanotechnology and respective application fields (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

and Chevron—all active in the oil industry—belong to the category hydrocarbon processing/cracking.

Furthermore, the assignee companies were analyzed regarding their location to determine the countries leading the field of industrial research in nanocatalysis as illustrated in Figure 8. Almost three-quarters of all patents in our sample were granted to companies located in the USA, followed by Japanese, Korean, and German companies. All countries with less than 20 patents were allocated to the category various. Of course, it should be borne in mind that the research was performed on the database of the US Patent and Trademark Office, which could lead to a minor bias toward American companies. Nevertheless, the analysis shows the strong technology position of the USA. Due to the terms specified by the Patent Cooperation Treaty (PCT) it is possible that innovations already granted in other member countries are still pending in the United States and are therefore not included in our search results.

After analyzing our entire sample of 475 patents regarding the years of granting, the application fields, and the assignees, we will show in the following part the percentage of porous nanocatalysts and nanoparticle catalysts, respectively. Furthermore, with regard to green chemistry, we searched for evidence whether the aspect of catalyst recovery is already considered in the patents. For these two analyses we used all the 246 patents that resulted from our full-text research on the US Patent and Trademark Office Patent Database, as described above.

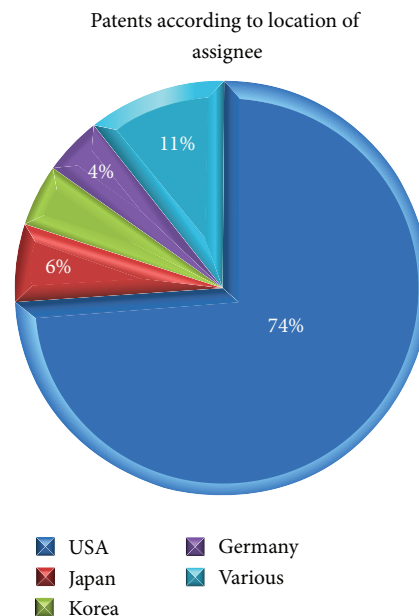


FIGURE 8: Overview of assignees' locations (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

As previously explained, there are two major categories of nanocatalysts: porous and particulate catalysts. Figure 9 illustrates that two-thirds of the nanocatalysts specified in the analyzed patents are of porous nature; that is, either the catalyst itself is porous or, alternatively, the catalyst is stabilized on a porous support. Nanoparticle catalysts are used according to 30 per cent of the patents and therefore obviously make up the minor part.

One reason for that is illustrated in Figure 10: almost all patents in the application field hydrocarbon processing/cracking and the majority of patents in the application field various chemical processes, which are the two largest categories, specify porous catalysts.

As we detailed earlier in the present paper, nanocatalysis is expected to contribute to the realization of the principles of green chemistry. Of course, the recovery and recycling of used catalysts are a cornerstone of the strategy toward a greener chemistry. As we analyzed the patents regarding this aspect, we observed that only 13.4 per cent of the patents in the sample mentioned a method to recover the nanocatalysts, as illustrated in Figure 11. Although the magnetic recovery of nanocatalysts is a hot topic in academic research, as inferred from various publications discussed above [22, 33, 50, 55, 56, 84, 85, 115–118, 140–142], only two patents (0.8%) suggest the use of magnetic recovery. The majority of all patents (65.4%) do not specify any kind of recovery method. For 21.1 per cent of the analyzed patents, the concept of nanocatalyst recovery is not readily applicable to the respective application, as for example, in the case of fuel cells, which should show long life spans anyway.

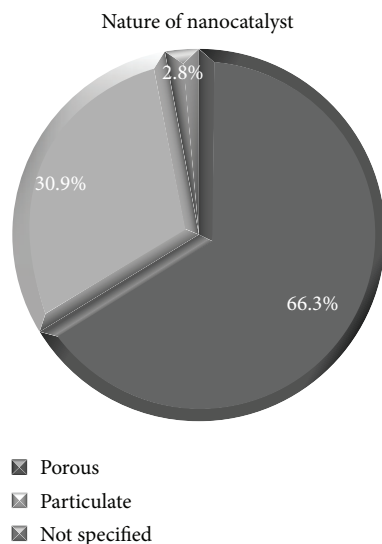


FIGURE 9: Nature of nanocatalysts described in the selected patents (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

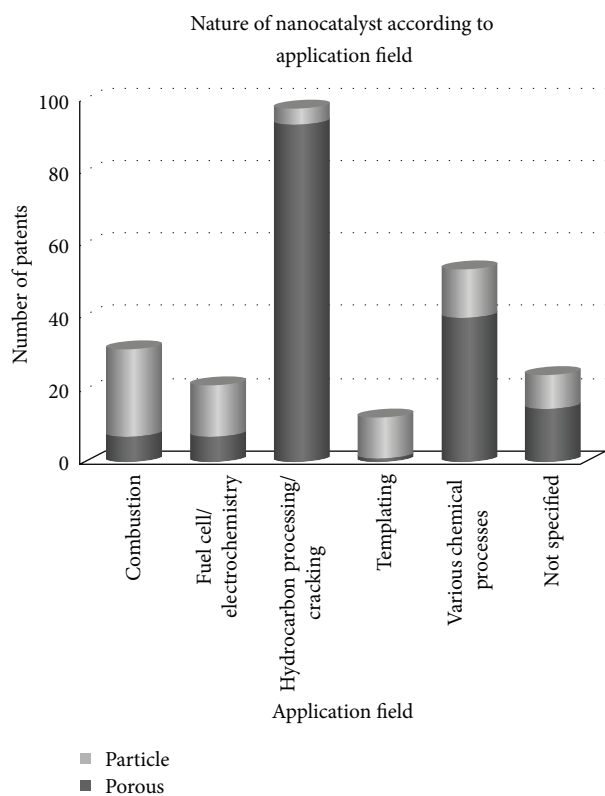


FIGURE 10: Proportion of nanoporous and nanoparticle catalysts used in the specified application fields (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

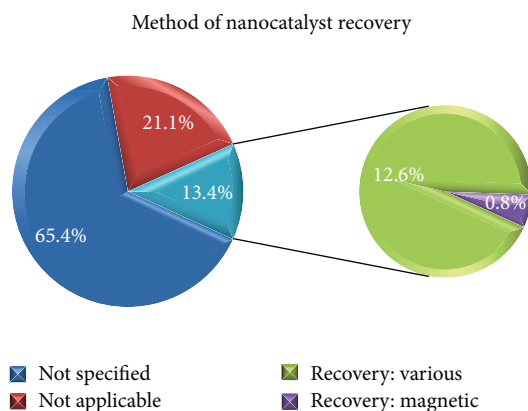


FIGURE 11: Recovery methods considered in patents related to nanocatalysis (based on a research on the US Patent and Trademark Office Patent Database (<http://patft.uspto.gov/>) applying the working definition stated in the beginning of this review).

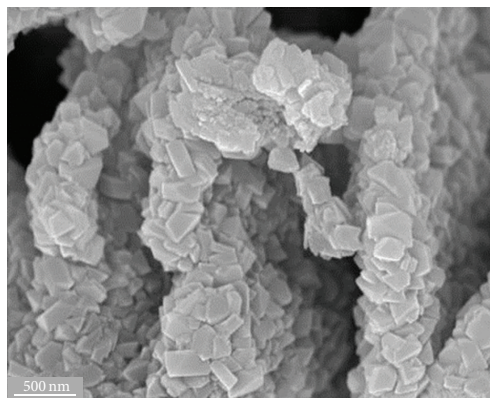


FIGURE 12: Scanning electron microscope pictures of BASF's Endurance nanocatalysts (obtained by and used with permission from BASF).

**5.2. Market Impact of Nanocatalysis.** The above discussion revealed both academic and industrial ventures into the field of nanocatalysis. To strengthen the assertion about its present and future importance, we will provide an insight into the market for nanocatalysis and its growth potential, and we will present selected players and products in the market. It should be noted that catalysts in general participate chiefly in a business to business (B2B) market and are therefore not as obvious to the nonprofessional observer as goods in a consumer market [17]. Nevertheless, according to The Freedonia Group, the global catalyst market had a remarkable size of USD 12.8 billion in 2009 and is forecast to grow 6 per cent annually to USD 18.2 billion in 2015 [167]. The three main segments are various chemical processes, oil refining, and environmental applications [16]. Narrowing down from the catalyst market in general to the market for nanocatalysts, the same optimistic trend can be observed: the market size can be calculated from the data provided by Zhou et al. [26] and Global Industry Analysts, Inc. [168] to about USD 4.5 billion in 2009. It makes up about 35 per cent of the entire



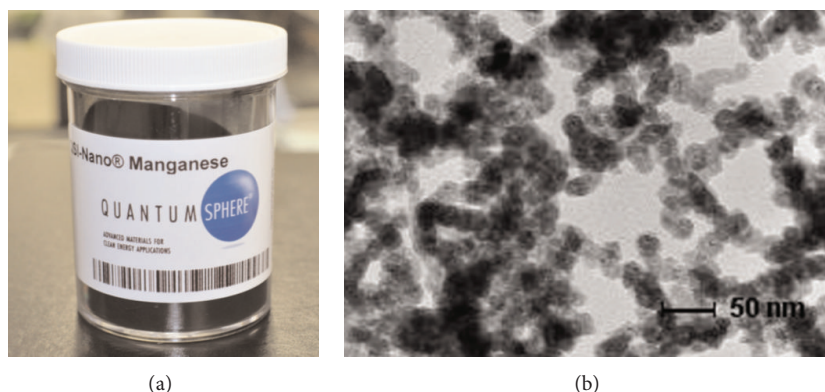


FIGURE 13: QuantumSphere's QSI-Nano Manganese catalyst powder (a) and electron microscope picture of the core-shell nanoparticles (b) [13] (used with permission from QuantumSphere Inc.).

catalyst market, corresponding to an estimate of the CEO of Catalyst Group, Inc., cited in Hu et al. [16]. Further, the market is forecast to grow with a compound annual growth rate (CAGR) of 5 per cent to about USD 6 billion in 2015 [168].

As can be expected, several large and well-known global corporations participate in this market, which was also reflected in our patent analysis (see Figure 7). Headwaters, Inc., for instance, offers the HCAT nanocatalysis technology for heavy oil upgrading. The highly dispersed catalyst enables an improved residue conversion from heavy asphaltene molecules to lighter hydrocarbons [169, 170]. Moreover, the company developed the NxCat system consisting of platinum-palladium nanoparticles for the commercialization of direct  $\text{H}_2\text{O}_2$  synthesis [16, 171]. A further big player in the industry, the German BASF, lists several nanocatalysts in its product portfolio. The HDXtra and the Endurance zeolitic nanocatalysts (Figure 12) are used in the field of fluid catalytic cracking. The former maximizes the formation of light cycle oil from heavy feedstock and the latter enhances the coke and gas selectivity leading to higher liquid yields [172].

A nanocatalyst for ammonia and hydrogen production was recently commercialized by the company Haldor Topsoe. The catalyst consisting of copper nanoparticles separated by metal oxide barriers strongly reduces the undesirable formation of methanol [173]. The BRIM technology employing a nickel molybdenum nanocatalyst is offered by the same company to prepare essentially sulfur free diesel [174].

ExxonMobil, the second largest company in the world according to the Standard & Poor's 500 index, developed a number of refining catalysts, for example, the EBMax technology. This zeolitic nanocatalyst is used in the selective production of ethylbenzene from benzene and ethylene [16].

Besides the numerous big players—some of them presented above—there are also small and medium corporations (SMEs) as well start-up companies participating in the market. Often, these companies play an important role in their respective technological niche market by offering highly innovative products. One of them is the US company QuantumSphere, which has several integrated nanocatalytic solutions in its portfolio [175]. For instance, they provide

a manganese core-shell nanocatalyst called QSI-Nano Manganese for use in fuel cells or chemical oxidation reactions (Figure 13) [13].

Furthermore, QSI-Nano Copper can be used as a highly active nanopowder catalyst in the production of methanol [176].

Another SME in the field, *nGimat*, offers metal oxide nanoparticle catalysts for hydrogen generation from hydrocarbon fuels, with high capacities and purities at low temperatures [177]. A catalytic templating process for the preparation of carbon nanotubes was developed by Molecular Nanosystems Inc. The technology of the start-up company is based on chemical vapor deposition on metal nanoparticles [178].

With regard to catalyst recovery, the Swiss start-up company TurboBeads LLC offers a product portfolio based on magnetically separable nanocatalysts (Figure 14). The basic principle of their technology is a magnetic nanoparticle that comes with various surface functionalizations (e.g., TurboBeads Amine, TurboBeads Carboxy, and TurboBeads Click) for the application in a multitude of different reaction fields [179].

## 6. Conclusion

The present paper provides a detailed insight into the field of nanocatalysis both from an academic point of view and an economic point of view. By reviewing current scientific literature on nanocatalysis in the first part of the paper we demonstrated its importance in academic research. Thereby, we discussed the advantages of nanocatalysis compared to the two conventional catalysis methods and we showed its potential to contribute to a greener chemistry. Furthermore, we presented the four dimensions that define catalyst performance and the three factors (size, shape, and surface composition), which can be influenced by recently developed synthesis methods. In that direction several examples for syntheses of high performance nanocatalysts and their potential future applications were provided.

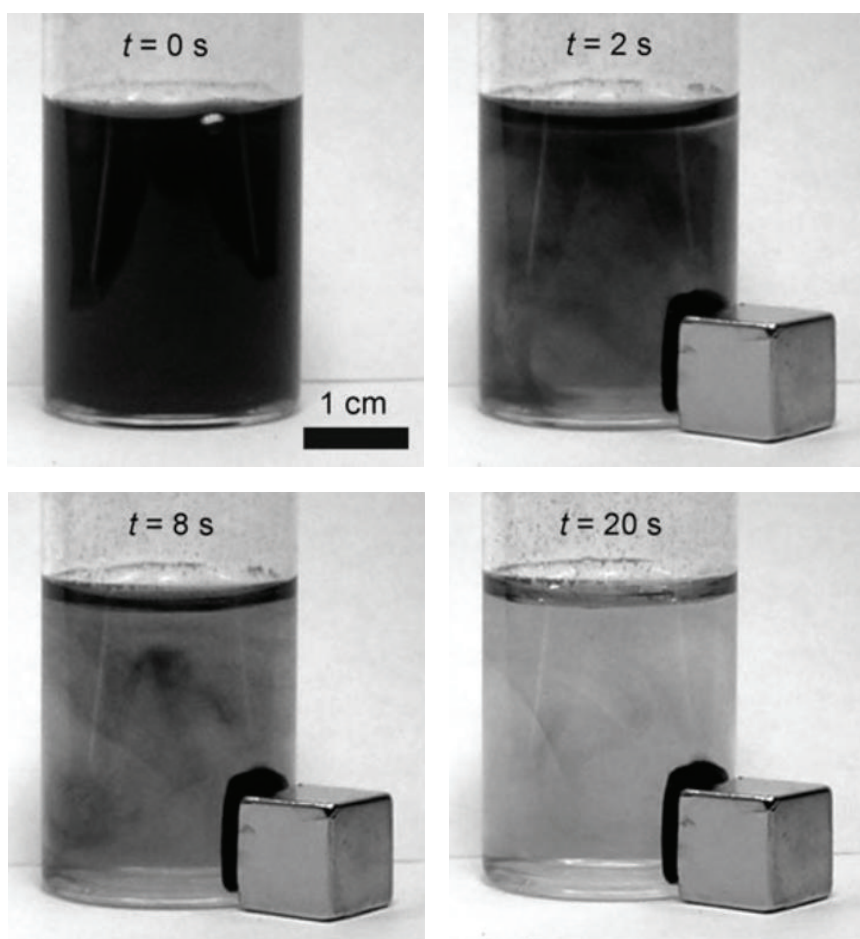


FIGURE 14: Magnetically separable nanocatalysts similar to those offered by TurboBeads [14] (used with permission from John Wiley and Sons).

Then we turned from future promises to the present by considering the technology situation of nanocatalysis. For that purpose, we performed an extensive patent search analyzing more than 1,500 patents. We found that the patents could be classified into six application fields (combustion, fuel cell/electrochemistry, hydrocarbon processing/cracking, templating, various chemical processes, and not specified) and that US companies hold a strong technology position in nanocatalysis. Furthermore, the analysis showed that, despite its prominence in academic research in the field, nanocatalyst recovery is not yet widely considered in the patents.

As nanocatalysis is a formidable example for a B2B market for nanotechnology, recent market data to show the current situation as well as growth perspectives to illustrate the future potential of nanocatalysis were presented. From the present review we conclude that nanocatalysis still offers a wide variety of opportunities for researchers, both in academia and in industry, to increase catalyst performance and to develop innovative and green chemical processes.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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